

Nonspherical Deformations of the Ions in Fluorite

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The structure amplitudes of CaF_2 measured by Togawa (J. Phys. Soc. Japan 19 (1964) 1969) are analyzed using methods developed by Kurki-Suonio (Ann. Acad. Sci. Fennicae A VI 93 (1962)). There is a considerable uncertainty in the scale and temperature parameters due to the residual term. The optimum values are slightly higher than those used by Togawa. The deviations of the ions from spherical symmetry are small but detectable. They can be characterized roughly by saying that the ions are slightly compressed by their nearest neighbours and extended towards the more empty regions, the fluorine ions also towards each other. The average trend of the experimental atomic factors coincides with the theoretical atomic factors within experimental errors.

§ 1. Introduction

Only non-approximate methods of analysis can be used if one wants to extract all information from very accurate experimental data. One of the authors has proposed for that purpose a possible plan to be followed.¹⁾ It has also been applied in a couple of cases.^{2,5)} It seemed us advisable to refine the analysis of Togawa's data⁶⁾ on fluorite along the same lines.

Fluorite has a cubic unit cell with the ionic positions

$$\left. \begin{array}{l} \text{Ca: } 0, 0, 0 \\ \text{F : } 1/4, 1/4, 1/4 \\ \text{F' : } 3/4, 3/4, 3/4 \end{array} \right\} \text{+face centred positions.}$$

According to the crystal symmetry all calcium ions are identical, the two different fluorines are related by inversion, hence $f_{\text{F}'} = f_{\text{F}}^*$. If only the symmetry determined by the crystal symmetry is assumed for each ion the structure amplitudes can be written as follows

$$\begin{array}{lll} hkl & h+k+l & 1/4 F_{hkl} \\ \text{all even} & 4n & f_{\text{Ca}} + 2\text{Re}f_{\text{F}} \\ \text{all even} & 4n+2 & f_{\text{Ca}} - 2\text{Re}f_{\text{F}} \\ \text{all odd} & 4n\pm 1 & f_{\text{Ca}} \pm 2\text{Im}f_{\text{F}} \\ \text{mixed} & - & 0 \end{array}$$

The theoretical atomic factor of Freeman⁷⁾ for Ca^{++} and that of Boys⁸⁾ for F^- were chosen for the basic model of the analysis. In order to find the theoretical values at each κ ($=\sin\theta/\lambda$) we used the analytic approximations

$$f \sim \sum_i A_i e^{-a_i \kappa^2}, \quad (1)$$

with the parameters given in Table I for the theoretical atomic factors at zero temperature, and interpolated the remaining differences graphically.

Table I. Values of parameters used for the analytic approximation of the theoretical atomic factors.

	A_1	a_1	A_2	a_2	A_3	a_3
f_{Ca}	9.900	0.84615	8.048	13.2727	—	—
f_{F^-}	3.925	1.60377	5.207	12.0425	0.8747	35.3086

As usual we let the ions of the model crystal undergo random harmonic oscillations which gives a Debye factor $e^{-B\kappa^2}$ to each of the ions. Because of the crystal symmetry B_{F} and B_{Ca} are constants independent of the crystallographic direction.

As experimental values we used the $\text{CuK}\alpha$ data of Togawa.⁶⁾ We applied the dispersion correction according to Cromer⁹⁾ and used the lattice parameter $a=5.4626 \text{ \AA}$. The Chipman factor¹⁰⁾ (the temperature diffuse scattering correction) will in this case have no effect on the results we are going to calculate, and we shall omit it.

§ 2. Analysis

At first we calculated the Fourier difference series along the diagonal of the unit cell. The results are shown in Fig. 1. The first curve was found using parameters $B_{\text{Ca}}=0.637 \text{ \AA}^2$, $B_{\text{F}}=0.741 \text{ \AA}^2$ given by Togawa. For the second curve we used $B_{\text{Ca}}=0.668 \text{ \AA}^2$, $B_{\text{F}}=0.815 \text{ \AA}^2$. The third one was obtained with a scale higher by 2% and with the temperature parameters correspondingly adjusted to $B_{\text{Ca}}=0.578 \text{ \AA}^2$, $B_{\text{F}}=0.761 \text{ \AA}^2$, and it shows the effect of scale changes on the information included in the data.³⁾

The optimum values of the parameters are reached when the deviation of the experimental electron density from the model, i.e. the Fourier difference series, is as smooth as possible at the

atomic centres. This leads to the most natural continuation of the experimental atomic factors and thus to reasonable estimates for the residual terms if needed. According to this criterion the first curve of Fig. 1 indicates that the temperature parameters are too low, the second curve gives a slight suggestion of the original scale being also too low. In the further analysis we used the parameters of the third curve. The corresponding theoretical and experimental values are given in Table II. However, because of the small number of measured reflections there is a considerable uncertainty in these parameters.

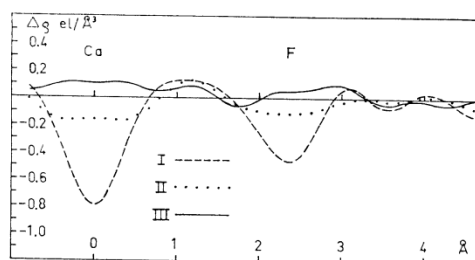


Fig. 1. Fourier difference series along the diagonal of the unit cell, I with the scale and temperature parameters according to Togawa, II with thermal parameters $B_{Ca}=0.668 \text{ \AA}^2$, $B_F=0.815 \text{ \AA}^2$ and III with the scale factor 1.02 and $B_{Ca}=0.578 \text{ \AA}^2$, $B_F=0.761 \text{ \AA}^2$.

Table II. The theoretical atomic factors at zero temperature. The dispersion corrected theoretical structure amplitudes F_{theor} with the thermal parameters $B_{Ca}=0.578$, $B_F=0.761$. The experimental values F_{exp} are obtained from Togawa's data using a scale factor 1.02 and the values F_{def} from F_{theor} by adding the corrections Δf_{Ca} , Δf_F calculated in the analysis.

hkl	κ	f_{Ca}	f_F	F_{theor}	F_{exp}	F_{def}
111	.1585	15.54	8.00	15.73	15.81	15.84
200	.1831	14.88	7.48	0.42		0.49
220	.2589	12.76	5.93	23.96	24.08	24.08
311	.3036	11.61	5.13	11.43	11.48	11.43
222	.3171	11.29	4.91	1.97		1.96
400	.3661	11.24	4.20	17.47	17.18	17.38
331	.3990	9.63	3.80	9.20	9.28	9.31
420	.4093	9.45	3.68	2.51		2.55
422	.4484	8.86	3.30	13.97	14.03	14.05
333	.4756	8.52	3.07	7.88	7.85	7.86
511	.4756	8.52	3.07	7.88	7.85	7.86
440	.5178	8.07	2.77	11.84	11.76	11.87
531	.5415	7.85	2.62	7.03	7.06	7.02
442	.5492	7.78	2.57	2.87		2.84
600	.5492	7.78	2.57	2.87		2.87
620	.5789	7.54	2.42	10.35	10.35	10.31
533	.6002	7.38	2.32	6.39	6.30	6.33

The experimental atomic factors can be calculated with the series

$$f_T(h, k, l) = \frac{1}{V_0} \sum_{h', k', l'} F_{hkl} \sigma_T(h-h', k-k', l-l), \quad (2)$$

which represents the scattering amplitude of a region T with the shape transform $\sigma_T(h, k, l)$. For each ion a natural choice of the region T will be a sphere centred at the ionic centre and with a radius equal to the ionic radius.

Actually we used the corresponding difference series to find the deviations of the experimental atomic factors from the theoretical ones. We used three different pairs of radii:

	R_{Ca}	R^F
1.	0.99 Å	1.36 Å
2.	1.12 Å	1.23 Å
3.	1.23 Å	1.12 Å

the sum of each pair being equal to the distance Ca-F. The first values are the classical ionic radii, which are too large for the negative ions and too small for the positive ones at least in the case of alkali halides.^{4,11} The second pair is chosen somewhat arbitrarily, but we believe it to be the most reasonable one. The third pair, again, is the other extreme.

Figures 2 and 3 show for each of the spheres the resulting Δf_{Ca} and Δf_F in the three main di-

rections $h00$, $hh0$ and hhh . In Fig. 4 the imaginary part of Δf_F is given separately for the second pair in hhh direction, in the other two directions it vanishes by symmetry. The dotted curves in Figs. 2b and 3b are calculated using the original scale with adjusted temperature factors (cor-

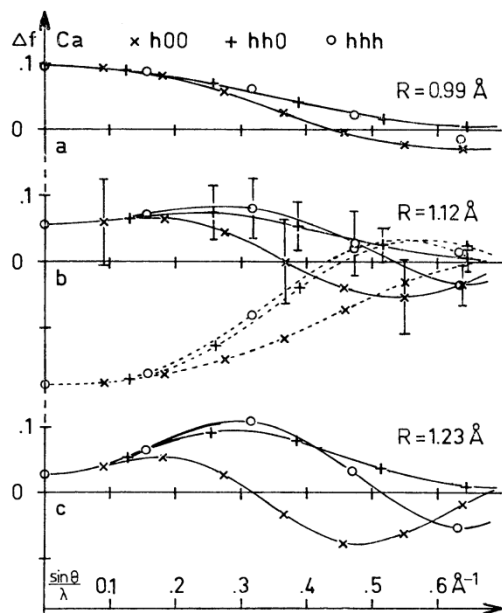


Fig. 2. The difference between the experimental and theoretical atomic factor of the calcium ion calculated in main crystallographic directions using three spheres of different sizes. The dotted curves are obtained with the original scale which was lower by 2%.

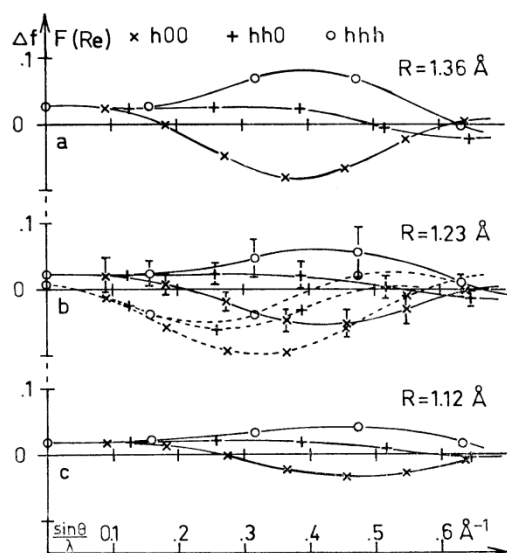


Fig. 3. The real part of the difference between the experimental and theoretical atomic factor of the fluorine ion calculated in main crystallographic directions using three spheres of different sizes. The dotted curves are obtained with the original scale.

responding to the second curve in Fig. 1), and are aimed to demonstrate the effect of changing the scale.

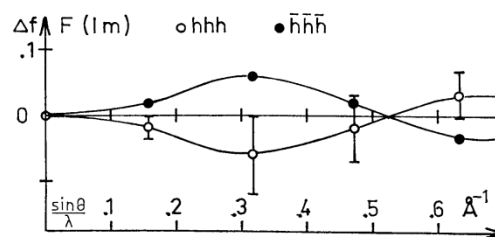


Fig. 4. The imaginary part of the experimental atomic factor of the fluorine ion F (at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) calculated using a sphere of radius $R=1.23 \text{ \AA}$.

The effect of experimental errors was estimated assuming for each of the experimental structure amplitudes a standard deviation 0.07, which is about the average of the limits of error given by Togawa. The corresponding standard deviations of the results are marked in the figures for some of the points. The standard deviations of the differences between the curves in different directions are of about the same magnitude as those of the individual curves. To make sure, we calculated it for the difference $\Delta f_F(500) - \Delta f_F(333)$ and found 0.048 for $R=1.23 \text{ \AA}$ and 0.032 for $R=1.12 \text{ \AA}$.

§ 3. Results and Discussion

The magnitude of these differences is more or less a measure for the number of electrons, which have to move in order to produce the deformation. The differences are almost independent of the temperature parameters and of the scale as well as of the choice of the theoretical atomic factors. To judge their significance we therefore have to take into account only the experimental errors and the effect of the unmeasured reflections below the cut off limit of κ .

If compared with the standard deviations due to experimental errors only, the differences are not strong but still significant. They are clearly insignificant only for the smallest sphere for calcium.

The omission of the weak reflections in the difference series is identical with having their experimental structure amplitudes equal to the theoretical ones. Because the theoretical values are based on spherically symmetric atoms this will make the deformations appear smaller than they actually are. Therefore the significance of the deformations is not at least reduced.

This all holds also for the imaginary part of Δf_F , although it has rather weak significance.

From the general behaviour of the Δf curves we can conclude some qualitative features of the deformations.

If we follow the development of the differences of the Δf curves in different directions, with growing radius, in Figs. 2, 3, we can make the following general observations: There is no detectable deviation from spherical symmetry in the calcium ion inside the classical radius $R=0.99 \text{ \AA}$, since the differences of the curves in Fig. 2a are completely insignificant. The differences seen in Figs. 2b, c must therefore come from slight deformations outside this part. In fluorine there is some trace of the deformation still left in the smallest sphere (Fig. 3c). In the larger regions, Figs. 3a, b, the differences are slightly greater than at the calcium ion and clearly more significant. So, the deformation in fluorine is slightly stronger and the deformed layer is thicker, in spite of the much smaller number of electrons. We could characterize this situation by saying that the fluorine ion is more deformable than calcium.

As to the geometry of the deformation, the differences of the Δf curves indicate that the Calcium ion (at 0, 0, 0) is slightly compressed both by the neighbouring fluorine ions (at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ etc.) and by the nearest calcium ions (at $\frac{1}{2}, \frac{1}{2}, 0$ etc.) as shown by its Δf curves in the directions hhh and $hh0$ respectively, when compared with

the behaviour in the more empty $h00$ direction. The Δf curves of the fluorine ion F (at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), including the imaginary part, indicate that the ion is compressed by the neighbouring calcium ions (at 0, 0, 0 etc.) and extended towards the empty regions on the opposite side and also towards the other fluorines F' (at $-\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; $\frac{3}{4}, \frac{1}{4}, \frac{1}{4}$ etc.) These features are shown in a more concrete manner in Fig. 5. It represents for the second pair of ionic spheres the difference Δf between the experimental and theoretical electron densities as projections on main crystallographic directions. The curves are just one dimensional Fourier transforms of the (complex) function Δf represented by the solid curves in Figs. 2b, 3b and 4, and they were easily obtained with help of an analog computer.

The terminology used above must be understood exclusively as a characterization of the geometry of the effect without any reference to its origin, whether it is static or dynamic for instance.

All these qualitative features are quite natural for simple physical reasons. They are also very similar to the results found for some other ionic crystals^{4,12)} and agree qualitatively with the results of Weiss *et al.*¹³⁾

The results of Willis¹⁴⁾ reveal an unharmonicity in the motion of the fluorine atoms (or something equivalent). This also would give rise to an imaginary part in hhh direction. However, the effect reported by him would not be visible at all at the present values of ϵ . The imaginary part shown in Fig. 4 is mainly due to effects in the outer parts of the atom.

The values F_{def} given in the last column of Table II are obtained by making in the theoretical atomic factors the corrections Δf found with the second pair of spheres. The remaining differences $F_{\text{exp}} - F_{\text{def}}$ obviously do not contain any more information concerning these regions. As we see, the effect on any single reflection is only of the order of experimental errors, and there can hardly be seen any improvement. In Δf the deformations mean numerically so little that it would be impossible to detect them with help of a Fourier analysis, where the termination effects spoil the picture, but still there are enough of electrons taking part to the effect as a whole to make it detectable in the reciprocal hkl space, where we keep in our analysis.

The possibility of obtaining such small deviations from spherical symmetry is essentially

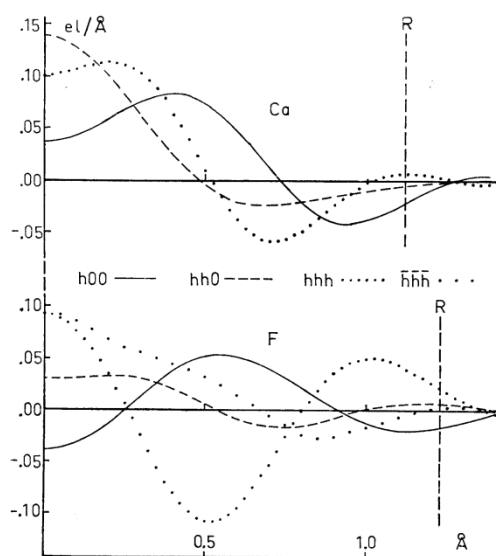


Fig. 5. One dimensional Fourier transforms of the differences between the experimental and theoretical atomic factors in main crystallographic directions represented by the curves in Figs. 2b, 3b, 4.

based on the fact that this particular kind of information is very insensitive to the choice of the theoretical atomic factors, to the uncertainty in the scale and the temperature parameters, and to the residual term problem, which all have spherically symmetric effects on the individual atoms, except second order corrections. Instead, results concerning the average trend of the atomic scattering factors are strongly effected by all these sources of uncertainty. Therefore it will be much more difficult to deal with such questions as the reliability of the theoretical atomic factors, the ionic states of the atoms, the correct values of the scale factor and the temperature parameters etc., which all are coupled together and to the residual term problem.

However, if we can trust in the criterion used for fixing the scale and the temperature factors, we can say that inside the ionic spheres the average trend of the electron density coincides with the theoretical atoms within the limits of experimental errors. If we cannot, we neither have anything else to be based on and the statement is still valid. For more accurate information of these problems the experimental data ought to be extended to higher values of κ .

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